

CHAPTER 4

Results and discussion

4.1 INTRODUCTION

This chapter is structured in five parts. Firstly experimental results from this research and theoretical filling emission calculations, using South African product (petrol) data, are presented. Thereafter experimental filling emissions for the Engen-Wentworth facility are calculated, based on the data collected. Finally observations made during data collection and the effective inclusion into future legislation for VOC emission control in South Africa are discussed.

4.2 EXPERIMENTAL RESULTS

Only the tankers that connected to the vapour recovery system during the time when data was collected (October 2002 and May 2003) are presented in Appendix E and will be used in determining experimental filling emissions (Section 4.4). The petrol loading data from Appendix E were converted to volumetric flows, as the volume loaded over a certain time was known. As the temperature of the fuel that was loaded was also known, an average product temperature for all the available data (that was used in the calculation of the theoretical and experimental filling emission calculations) was determined as 26,2°C.

The vapour flow (in m/s, measured by the ultrasonic flow meter), being a mixture of VOCs and air, was converted to one minute averaged volumetric flow values in Appendix F (only part of the measured data, the rest of the converted data is shown in Appendix G).

The typical vapour VOC concentration at the Engen facility had to be known before the experimental filling emission could be determined (the ultrasonic flow meter measures the velocity of the VOC/air mixture in the vapour header and the filling emission calculations are based on the VOC quantity). There were 2 paths through which the VOC concentration could be determined:

- i) experimentally *via* analysis of vapour samples from the Engen facility, and
- ii) theoretically, by using vapour pressure data.

Although direct measurement of the VOC concentration would be preferable, this option was too costly for this research and therefore grab vapour samples (using thermal tubes and glass samplers) were analysed to determine the VOC concentration. The analytical VOC concentration results for the grab samples taken from the vapour header at the Engen facility are shown in Appendix H.

The VOC concentration results of samples 1 to 4 (thermal tubes) were very low compared to the VOC concentration of 40 vol% value stated in Section 2.1 for European conditions. The highest VOC concentration was in sample 4 and was equal to 6497,32 ppm or 0,65 vol%; as shown in Table H.1 in Appendix H. According to Carr (2003), there could have been a breakthrough of the thermal tubes explaining the low results. So, even if the VOC concentration could have been high, the thermal tubes are only able to sample a limited amount and therefore the use of another sampling method had to be investigated.

Further research revealed that glass samplers, where a larger volume of vapour could be sampled, were a better alternative than the thermal tubes (Mey, 2003). Thermal tubes are more commonly used for ambient air samples and are designed for the adsorption of heavier hydrocarbons (VOCs) in low concentrations. Glass samplers will tend to understate the lighter hydrocarbons (VOCs), but a larger sample can be taken. Four samples were taken with glass samplers on the same day, a few minutes apart. As shown in Table H.3 the

results of samples 5 to 8 are higher than those of samples 1 to 4. The highest VOC concentration was for sample 5 and was equal to 11,07 vol %.

From the analysis the average molecular weight was also determined. For samples 1 to 4 (81,1 g/mol, Table 4.1) it was much higher than the European value of 64 g/mol, whereas the average result from samples 5 to 7 (59,5 g/mol) was in the same range as the European value. The average molecular weight of all eight samples was 70,3 g/mol.

Table 4.1 Comparison of average molecular weights of vapour samples (only VOC part) taken at Engen facility.

Samples 1-4 (thermal tubes)		Samples 5-8 (glas samplers)	
Component	Molecular weight %	Component	Molecular weight %
Methane	0,06	Methane	0,11
		Ethane and ethylene	0,36
Propane	1,16	Propane and propylene	6,36
Butane	8,44	Iso-butane	13,17
		1-butene	3,06
		n-butane	11,93
		t-butene-2	1,86
		c-butene-2	1,52
Pentane	11,11	Iso-pentane	0,03
		n-pentane	15,03
		1-pentene	0,39
		Pentane	4,35
Hexane	47,93	Iso-hexane	0,39
		n-hexane	0,29
Heptane	5,52	Iso-heptane	0,51
		n-heptane	0,03
Octane	3,36	Iso-octane	0,09
		n-octane	0,00
Nonane	2,49	Iso-nonane	0,01
		n-nonane	0,00
Decane	0,54	Iso-decane	0,00
Undecane	0,23	n-decane	0,00
Average molecular weight (VOCs only) g/mol	81,1		59,5

There could be various reasons for the low VOC concentration results. Every effort was made to ensure that mostly petrol was being loaded at the times when the samples were taken, but it is possible that other products could also have been loaded at this time, as the previous contents of the road tankers were unknown. It is thus possible that vapour originating from other product (for example diesel, resulting in very low VOC concentrations) could have been sampled, even though petrol was loaded. All the samples were taken as grab samples and this could also explain the low results if the samples were taken at times when the VOC concentration was low. All of the samples were taken at times when there were numerous tankers loading simultaneously.

Due to the low VOC concentration results from the analyses, it was decided to investigate the calculation of the VOC concentration theoretically. Assuming a state of equilibrium in the vapour space in the road tanker, it is known that the mixture of petrol vapour and air will be present at a constant ratio and the concentration of the petrol (VOC) vapour is proportional to the true vapour pressure (TVP) of the liquid petrol at its storage temperature (Hadley *et al.*, 1978:14). The petrol vapour displaces air, creating a partial pressure equal to the TVP, the balance of the partial pressure, assuming atmospheric pressure of 101,325 kPa, is due to the remaining air.

Using the nomogram (Figure B.1) in Appendix B, the TVP can be determined if the Reid vapour pressure (RVP) and the storage temperature of the petrol is known. For example, petrol with an RVP of 65 kPa at 37,8°C (100°F) will exert a TVP of 47 kPa at a storage temperature of 25°C (Figure B.1, Appendix B). The VOC concentration in the vapour space is then given by Equation 2 (assuming the vapour is 100% saturated at the conditions stated):

$$\text{VOC vapour} = \frac{47\text{kPa}}{101,325\text{kPa}} = 46 \text{ vol\%} \quad [2]$$

If the vapour is not fully saturated (as an example, only 40% saturated), the concentration will be given by Equation 3:

$$\text{VOC vapour} = 46 \text{ vol\%} \times 0,4 = 18 \text{ vol\%} \quad [3]$$

Using the nomogram in Appendix B and an S value (see Figure B.1 in Appendix B) of 3 for petrol (shown as motor gasoline in Figure B.1), values for TVP was determined for known RVP and temperature values. Figure 4.1 shows the resultant TVP values at different RVP and temperature values (with a linear relationship between TVP and RVP).

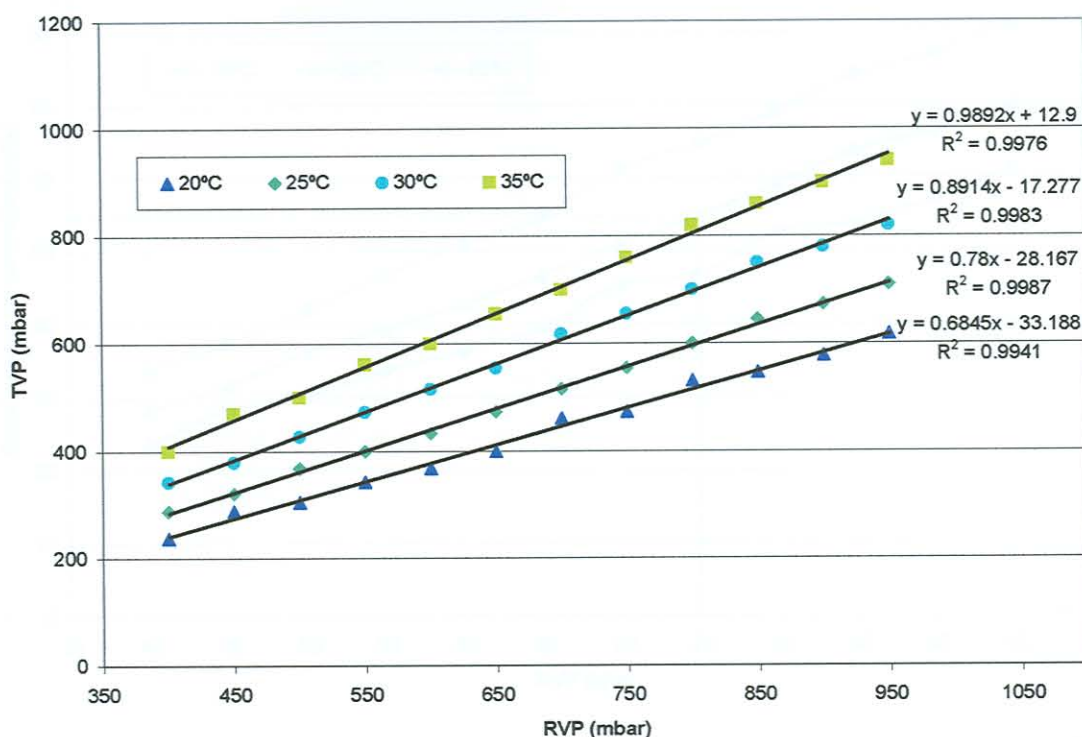


Figure 4.1 TVP versus RVP at temperatures from 20°C to 35°C.

Using Equation 2 and the TVP values determined for Figure 4.1, VOC concentrations were calculated for different RVP and temperature values. Figure 4.2 shows the theoretical VOC concentration of petrol vapour as a function of RVP and temperature, assuming the vapour is 100% saturated.

From Figure 4.2 the VOC concentration in the vapour increases with an increase in RVP, as well as temperature. As it cannot be assumed that the petrol vapour in the road tankers is saturated, Figure 4.2 can only give an indication of the relationship between RVP, temperature and concentration; and cannot be used to determine an average concentration at the Engen facility. It does, however, show the maximum possible concentration if the RVP and storage temperature of liquid petrol is known. At an RVP of 75 kPa (maximum allowable RVP in South Africa) and 25°C (typical storage temperature), the maximum possible VOC concentration will be in the order of 55 vol% (see Figure 4.2).

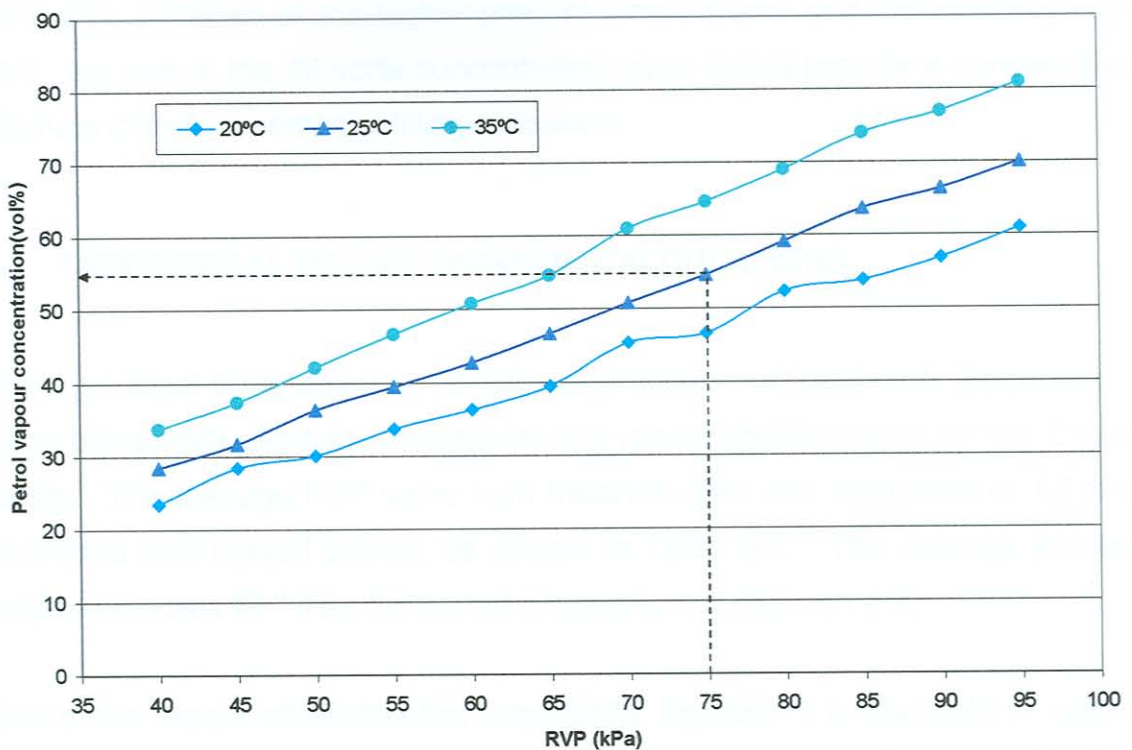


Figure 4.2 Theoretical VOC vapour concentration (vol%), assuming 100% saturation, as a function of RVP (kPa) and temperature.

Figure D.1 in Appendix D shows typical VOC concentration data at various temperatures for European summers (RVP = 70 kPa) and winters (RVP = 90 kPa) petrol. These are results from analysis on vapour samples taken by Cool Sorption (2001) in Europe. From Figure D.1 it can be shown that the typical

European VOC concentration is between 30 vol% and 40 vol% at a temperature of 15°C for petrol with a RVP of 70 kPa and 90 kPa, respectively. At a temperature of 25°C and using winter petrol data (RVP = 70 kPa), which is comparable to the RVP at the Engen facility, the VOC concentration is 40 vol% and at 30°C the concentration can be as high as 50 vol%.

Table 4.2 shows a comparison of factor f determined for the two sets of samples.

Due to the low VOC concentration results it was decided to use the value of 40 vol% for further calculations (Section 2.1). This value is a good approximation of the VOC concentration and has been proven to be correct under European conditions. As the VOC concentration in petrol vapour at the Engen facility would be higher, because of the higher product temperatures and the relatively high RVP, the use of the 40 vol% concentration value would provide a conservative estimate of the experimental filling emissions.

the most conservative estimate of filling emissions

4.3 THEORETICAL FILLING EMISSION CALCULATIONS

Table 4.2 Comparison of factor f determined for the two sets of samples

The theoretical filling emission is calculated based on Equation 1 (Section 2.2) using petrol RVP, product temperature and vapour characteristics for the Engen facility. The average RVP value from historical data was calculated as 65 kPa (unleaded and leaded petrol), as shown in Table 3.1. The average product temperature was 26 °C for the period of assessment (Section 4.2).

One of the vapour characteristics required for Equation 1 is the liquid to vapour equivalence factor f , derived in Appendix A for European conditions, and had to be adapted for the conditions at the Engen facility. Calculation of f required the average VOC molecular weight, liquid vapour density, product temperature and pressure at the Engen facility.

Figure 3.1 in Appendix B, if the RVP and product temperature is known. C_p is the preloading VOC concentration and is dependent

From Section 4.2 the average VOC molecular weight was 81,1 g/mol and 59,5 g/mol for samples 1 to 4 and 5 to 8 respectively. The liquid vapour density was not determined experimentally and therefore the same value as in Appendix A

was used. According to Hadley *et al.* (1978:43), the liquid vapour density (only VOCs) is 600 kg/m³ at 15°C and 101,325 kPa. Average product temperature for the period of assessment was 26°C and an atmospheric pressure of 101,325 kPa was used in calculations.

Table 4.2 shows a comparison of factor *f* determined for the two sets of samples. The value of *f* determined with a molecular weight of 81,1 g/mol at 26°C is higher than the European value of 0,0045 at 15°C. The molecular weight of the second group of samples provided a lower value for *f*. Due to the large discrepancy between the experimental VOC concentration results, it was decided to use the *f* value from samples 5 to 8 (namely 0,0041 or 0,41%) for further calculations. Although this is slightly lower than the value derived for European data, it is expected that this represents a minimum value at the Engen facility, indicating the most conservative estimate of filling emissions.

Table 4.2 Comparison of factor *f* determined for the two sets of samples.

Variable	Results for samples 1 to 4	Results for samples 5 to 8
Molecular weight of vapour	81,1 g/mol	59,5 g/mol
Vapour density (in liquid form)	600 kg/m ³	600 kg/m ³
Storage temperature	26 °C (299 K)	26 °C (299 K)
Atmospheric pressure	101,325 kPa	101,325 kPa
f	0,0055	0,0041
V/L ratio	182	247

The other variables used in Equation 1 were *C_s*, *C_p* and *V_B*. *C_s* is the VOC vapour concentration at 100% saturation and is equal to the petrol TVP (Section 2.2). It can be determined from Figure B.1 in Appendix B, if the RVP and product temperature is known. *C_p* is the preloading VOC concentration and is dependent on the amount of product discharges that were made until a tanker was loaded again. For calculation purposes it was decided to assume that a road tanker will only discharge its contents at one point, and therefore *C_p* equals 0,15. The type

of loading method also has an influence on the amount of evaporation that would occur and because all the tankers at the Engen facility use bottom loading, a V_B value of 0,13 will be used for calculations (the average value for bottom loading, as explained in Section 2.2).

As the RVP and temperature of the product may vary, thereby influencing the amount of VOCs that evaporate, it was decided to determine filling emissions within an RVP range, rather than using the average value of 65 kPa (Section 3.3). As 75 kPa is the maximum allowable RVP for leaded and unleaded petrol, and because the RVP is almost always above 60 kPa (Section 3.3); a range of between 60 kPa to 75 kPa was used. The product temperature of the fuel can also vary between 20°C to 35°C (see Appendix E), and was therefore used as the product storage temperature range.

Figure 4.3 shows the theoretical filling emission (E_f) results for RVPs from 60 kPa to 75 kPa and for product temperatures from 25°C to 35°C. As expected, filling emissions increase with an increase in RVP and temperature. At an RVP of 65 kPa and 26°C, typical conditions at the Engen facility, the theoretical filling emission is approximately 0,08%. The results in Figure 4.3 give a good indication of the approximate amount of filling emissions that may occur and shows that the expected filling emissions at the Engen facility will be higher than the value of 0,05% stated by Hadley *et al.* (1978:48), for typical filling emissions under European conditions. As filling emissions are expressed as a percentage (Section 2.2), this means that for every 1 000 litres of petrol that is loaded at the Engen facility, 0,8 litres will evaporate.

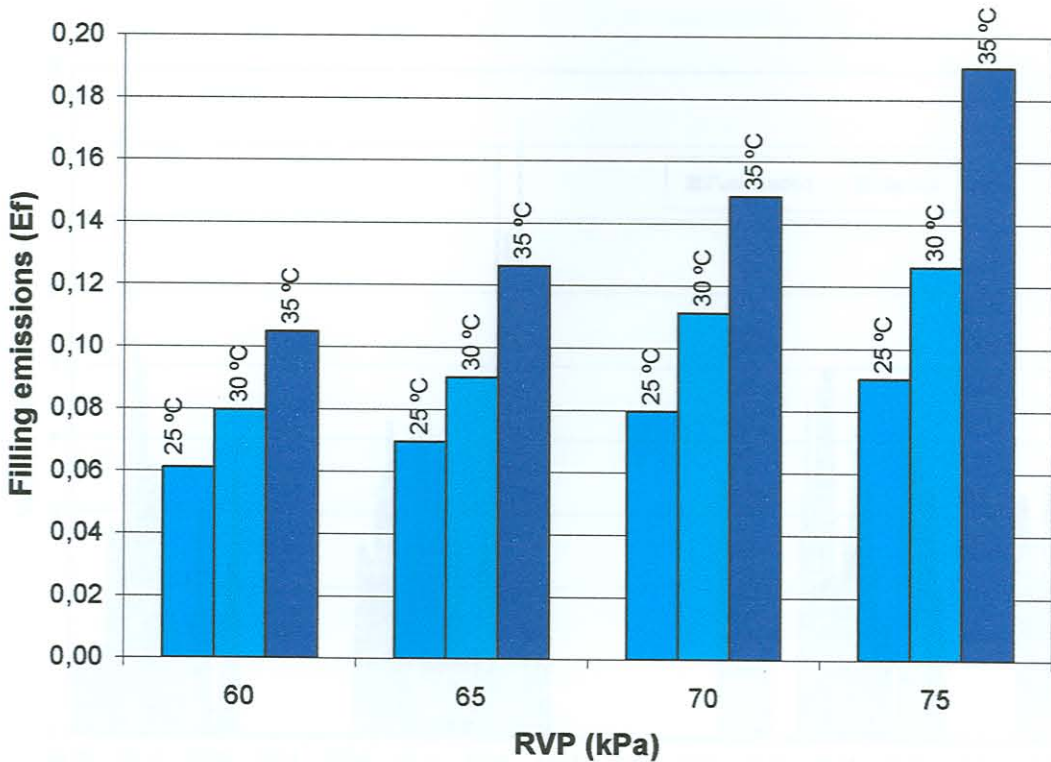


Figure 4.3 Filling emissions (E_f) for the typical range of RVPs and temperatures at the Engen, Wentworth facility (E_f is the liquid equivalent volume of VOCs in the vapour divided by the volume of petrol loaded, expressed as a percentage).

4.4 EXPERIMENTAL FILLING EMISSIONS

The petrol loading data (Appendix E) and the vapour flowrate data (Appendix F and G) were used to determine the experimental filling emission. As an example of the actual data collected, the fuel flow (petrol and diesel) and the corresponding vapour flow for tankers 28 to 44 during the period 08:09 to 14:01 on 6 May 2003 are presented in Figure 4.4. (Appendix I show similar examples during different days). Although some form of visual correlation does exist (apart from data for the first hour due to operational problems, see Section 4.5), the following aspects may impact on obtaining good correlations between loading and emission rates.

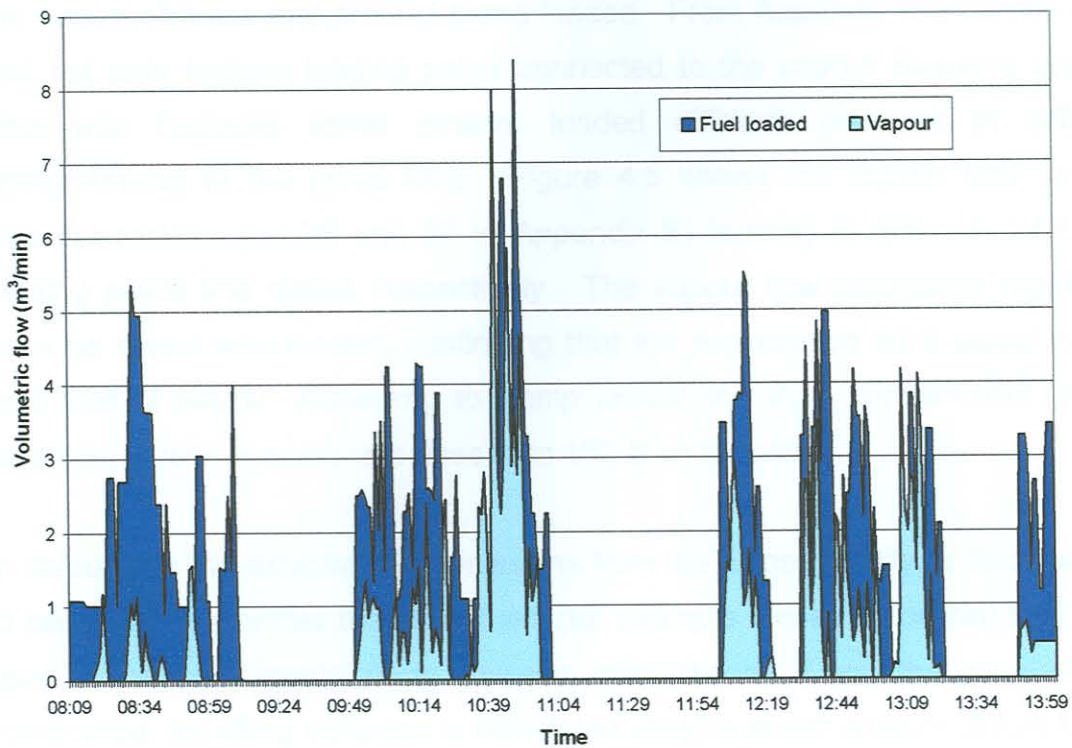


Figure 4.4 Comparison between fuel loading data and vapour flow through the vapour header for the period 08:09 to 14:01 on 6 May 2003.

As the actual vapour flowrate through the vapour header will be dependent on the overall loading rates at all the loading bays, loading characteristics will impact on final vapour flowrates. For example, when fuel is loaded, the first and last hundred litres of a loading start and finish slow, to prevent overfilling (Hamilton, 2002). This then results in plug flows through the vapour header, which would explain the numerous peaks in Figure 4.4. The design of road tankers will also determine the rate at which fuel is loaded (for example, some tankers are capable to load at about 2 200 litres per minute; while others may only load at 1 600 litres per minute). The number of tankers loading at the same time will also result in changing flowrates due to overall loss of pressure over the loading bays (Hamilton, 2002).

The other aspect that impacts on the VOC concentration and vapour flowrate is the nature of the actual product being loaded. From Appendix E it can be seen that not only tankers loading petrol connected to the vapour recovery system. This was because some tankers loaded different products in different compartments at the same time. Figure 4.5 shows the vapour flow for two different tankers (no 36 and 37 in Appendix E) loading at different bays and loading petrol and diesel, respectively. The vapour flow decreases rapidly as soon as diesel was loaded, confirming that the evaporation from diesel is less than that of petrol. According to Kemp (2003) the VOC concentration in, for example, diesel, is much less (less than 1%) than for petrol.

In calculating the experimental emissions from the Engen facility, a decision had to be made on whether the other fuels (for example diesel, kerosene) had to be used in the experimental filling emission calculations. If only the petrol data is considered, the filling emission is calculated using a lesser amount of fuel for the same vapour data and it is then assumed that all the vapour is petrol vapour with a VOC concentration of 40 vol%, which in the case of diesel vapour, is not true. Therefore, by using the total amount of fuel loaded, the effect of the vapour that may have originated from diesel (therefore, very low VOC concentration) is compensated for. On the other hand, the previous tanker contents could have been petrol, therefore contributing to the VOCs in the vapour, but the other fuels only contributed to a small percentage of the total fuel loaded during this time. There will be a VOC/air flow from trucks loading diesel, but most of the vapour measured were from tankers loading petrol. It was therefore decided to show the experimental filling emission calculation for both situations. The calculation used to determine the experimental filling emission follows as an example.

The results from the data collected during different days in October 2007 and May 2003 are shown in Table 4.3. In the first column only the petrol loading data and all the vapour data was considered and it was assumed that all the vapour measured by the ultrasonic flowmeter was from petrol. All the other fuel loaded was ignored. The second column is the filling emission if all the fuel's loading

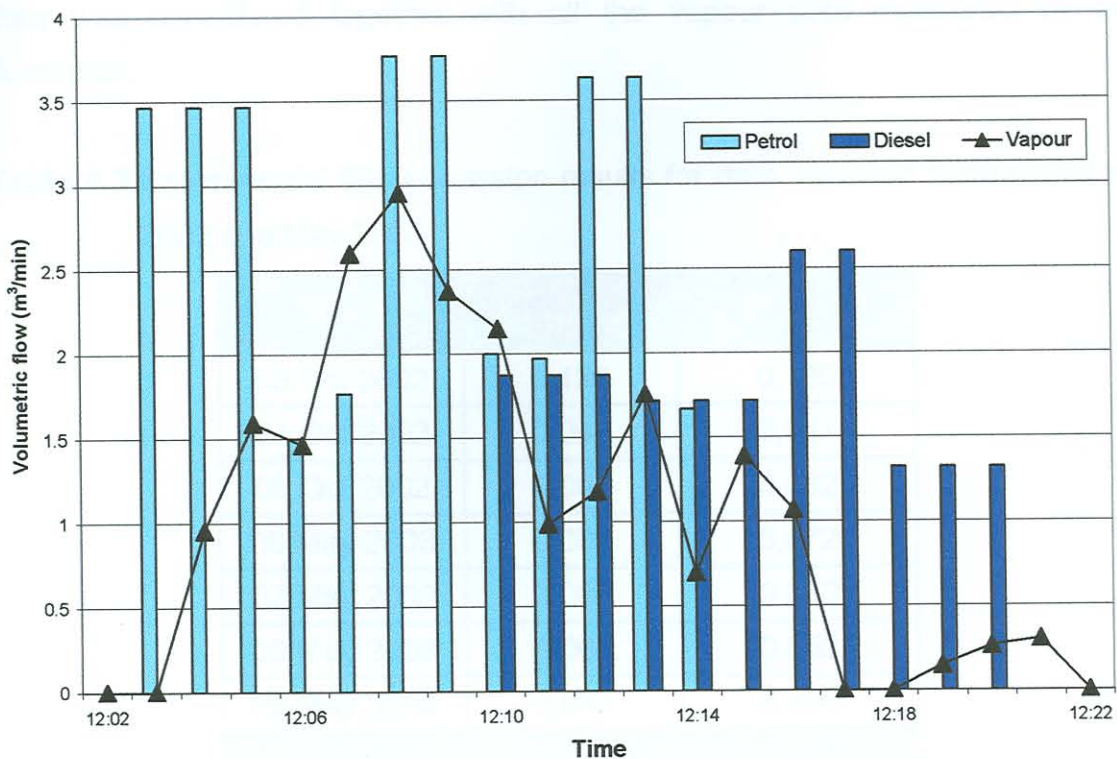


Figure 4.5 Vapour flow over a time period where petrol and diesel were loaded into two different tankers.

Say there is $P \text{ m}^3$ petrol that is loaded and $V \text{ m}^3$ vapour evaporates, where the vapour is a mixture of VOCs and air and the VOC concentration is 40 vol % (Section 4.2). The liquid to vapour volume equivalence value, f , for petrol was determined at the Engen facility as 0,0041 (Table 4.2). The actual emission E_f can then be calculated using Equation 4.

$$E_f = \frac{0,4 \times V \times f}{P} \times 100 \quad [4]$$

The results from the data collected during different days in October 2002 and May 2003 are shown in Table 4.3. In the first column only the petrol loading data and all the vapour data was considered and it was assumed that all the vapour measured by the ultrasonic flowmeter was from petrol. All the other fuel loaded was ignored. The second column is the filling emission if all the fuel's loading

data was considered together with all the vapour data measured by the flowmeter.

Table 4.3 Experimental filling emission results for data collected during October 2002 and May 2003.

Date	Filling emission	
	Petrol	Total Fuel
03 Oct 2002	0,139	0,139
04 Oct 2002	0,047	0,047
05 Oct 2002	0,082	0,082
06 May 2003	0,089	0,072
07 May 2003	0,094	0,070
08 May 2003	0,062	0,052
09 May 2003	0,041	0,030
Average	0,079	0,069

As shown in Table 4.3, when all the fuel loaded was taken into consideration, the average experimental filling emission from all the collected data was approximately 0,07%. Therefore for every 1 000 litres of petrol that is loaded into road tankers, 0,7 litres evaporate. When only petrol is considered the filling emission is higher (0,08%). As most of the fuel loaded during the time of this research was petrol the experimental filling emission was taken as 0,08%. This value is much higher compared to the value of 0,05% for European conditions.

The theoretical and the experimental filling emission results compare well although many assumptions were made in the calculation of the experimental filling emission calculations. The analytical results to determine the molecular weight from petrol vapour and the VOC concentration was the largest obstacle in the determination of the experimental filling emission, together with the fact that different fuels were loaded at the facility during data collection.

4.5 GENERAL OBSERVATIONS

During the time when the experimental data was collected, the general use of the vapour recovery equipment by the road tanker drivers was observed to assess any possible operational problems. Table 4.4 shows a list of the tankers where problems with vapour collection did occur.

At the Engen facility all tankers loading petrol must be adapted (as explained in Chapter 2) to allow for vapour return from the tankers to the VRU. Almost all the tankers loading at the Engen facility have been adapted and only one tanker (Tanker 2) out of over 100 tankers assessed, were not adapted for vapour collection.

At some stages during experimental data collection it was found that the vapour return hoses were filled with product (liquid petrol). This occurs when the overfill sensor on the tanker does not work properly and liquid petrol is pushed through the vapour return piping into the hoses when a compartment is full. This petrol is wasted as it is emptied into the drains on the facility. The tankers responsible for the overfilling were not known as the hoses were not checked after each tanker loaded.

In the case of tankers 28 and 62 in Table 4.4 the road tanker drivers were aware that their tanker's overfill sensors were not working. They then observed the level in a specific compartment through the manholes on top of the tankers. This involved the driver standing on the top of the tanker in order to stop the loading of fuel whenever a compartment is full. Even though these tankers were still connected to the vapour return system, it defeated the purpose as all the vapour escaped into the atmosphere through the open manholes.

Table 4.4 List of road tankers where problems with vapour collection did occur at the Engen facility.

Number (as indicated in Appendix E)	Tanker name and number	Observation
28	Unitrans (686)	Manhole on top of tanker is open, even though the tanker is connected to the vapour return system.
62	Bulktrans (24271)	Did not connect from the start of loading. Manhole on top of tanker is open even though tanker is connected to the vapour recovery system.
*	Freight Dynamics (372)	Not adapted for vapour return.
*	Engen Transport (96091)	Did not connect to vapour return system, although the tanker has been adapted for vapour recovery.

* Not shown in Appendix E because tanker did not connect to vapour return system, and was therefore not considered in calculations.

The effect on the vapour flow is illustrated in Figure 4.4, where from 08:09 to 08:20 there was no vapour through the vapour header and only Tanker 28 was connected to the system. After 08:20 there was a small amount of vapour measured, this was because the manholes were closed for a while during loading after instruction by the facility manager. At 08:31 Tanker 29 started loading petrol and the increased vapour flow can be seen in Figure 4.4.

4.6 INCLUSION IN SOUTH AFRICAN LEGISLATION

The newly proposed air pollution legislation, namely the Air Quality Bill (SA Bill, 2003) is aimed at replacing the Air Pollution Prevention Act (No 45 of 1965). The new legislation proposes the establishment of national norms and standards; a framework for air quality management planning and reporting; and regulatory

instruments for the control of air pollution and compliance and enforcement. The Air Quality Bill sets ambient air quality standards rather than emission standards. The draft bill also addresses various regulatory tools available to government for achieving acceptable ambient air quality, for example:

- *priority areas* may be identified for focussed attention;
- *listed activities* will have to require a licence before operation; and
- *controlled emitters*, where emission standards will be set for identified emitters.

The bulk storage of liquid petroleum products in storage facilities with individual tank capacities of at least 1 000 m³ is included as a scheduled process in the Atmospheric Pollution Prevention Act (No 45 of 1965). Although the CAPCO guidelines for hydrocarbon emission control requires that a programme of preventative maintenance must be implemented at all plants to minimise such emissions (CAPCO, s.a.), in practice these guidelines never resulted in the implementation of suitable vapour recovery systems. An example being that the Engen Wentworth vapour recovery system was the first of its kind to be installed in South Africa, and this only came into operation during 2001.

The draft bill on Air Quality does not mention the specific activities or areas that will be regulated, and therefore only the possible regulation of certain processes and areas can be discussed. The storage of petrol (and other petroleum products) could be extended to include smaller volumes as part of the new legislation, and then service stations storage tanks will also be included. The guidelines could also be altered to include the minimisation of VOC emissions during the distribution of petrol via recovery.

Transitional provision for ambient ozone and nitrogen oxide (NO_x) concentrations are made in the draft bill, but not for VOCs. As ozone is a secondary pollutant

formed when VOCs and nitrogen oxides (NO_x) react, VOCs will be regulated indirectly by the enforcement of the ozone standards.

Conclusions and recommendations

As discussed in Chapter 2, some European countries pre-empted the possibility of future legislation by installing vapour recovery systems before they were obligated to do so. This was also the case at the Engen-Wentworth facility. Internationally the control of VOCs from the storage and distribution of petrol (Stage I) has been applied for years and currently the focus is on the recovery of vapour from vehicle refuelling (Stage II). It is expected that the control of VOCs from petrol storage, distribution and refuelling in South Africa will be phased in over time, as was the case internationally.

Public pressure with regard to air pollution control will also play an important role in the application of vapour recovery in the future. In South Africa, communities are situated close to bulk storage facilities and public participation and awareness with regard to environmental matters, such as air quality, is increasing. An added advantage in the use of vapour recovery systems is the monetary value of the recovered VOCs, which makes this an attractive control option for the oil companies. The application of vapour recovery systems will also be easier to implement in South Africa, as the technologies have been proven and have been known internationally for some time.

For these reasons it is believed that an increase in the application of vapour recovery systems in South Africa will occur over a shorter period of time.